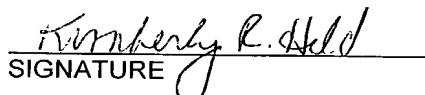


Form PTO-1390US DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE (Rev. 5-93) <b>TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371</b>		ATTORNEY'S DOCKET NO <b>H 4388 PCT/US</b>  U.S. APPLICATION NO (if known sec 17 CFR 1.5) <b>10/069409</b>
INTERNATIONAL APPLICATION NO. <b>PCT/EP00/07975</b>	INTERNATIONAL FILING DATE <b>August 16, 2000</b>	PRIORITY DATE CLAIMED <b>August 24, 1999</b>
<b>TITLE OF INVENTION</b> <b>MICROWAVE BONDING</b>		
<b>APPLICANT(S) FOR DO/EO/US</b> <b>Christian Kirsten, Dieter Dausmann, Uwe Franken, and Nikolaus Mathes</b>		
<p>Applicant herewith submits to the United States Designated/Elected Office (EO/DO/US) the following items and other information.</p> <ol style="list-style-type: none"> <li>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</li> <li>2. <input type="checkbox"/> This a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371</li> <li>3. <input type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39 (1)</li> <li>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date</li> <li>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)). <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau</li> <li>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US).</li> </ul> </li> <li>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2))</li> <li>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ul style="list-style-type: none"> <li>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</li> <li>b. <input type="checkbox"/> have been transmitted by the International Bureau</li> <li>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</li> <li>d. <input checked="" type="checkbox"/> have not been made and will not be made</li> </ul> </li> <li>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3))</li> <li>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)) <b>UNEXECUTED</b></li> <li>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5))</li> </ol> <p><b>Items 11. to 16. below concern other document(s) or information included:</b></p> <ol style="list-style-type: none"> <li>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</li> <li>12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included</li> <li>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment <ul style="list-style-type: none"> <li><input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment</li> </ul> </li> <li>14. <input type="checkbox"/> A substitute specification.</li> <li>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</li> <li>16. <input type="checkbox"/> Other items or information.: </li> </ol> <p>Version with Markings to Show Changes Made</p>		
<p>"Express Mail" mailing label number <b>EL615775349US</b></p>		

U.S. Application No. (If known see CFR 1.80) <b>107069409</b>	INTERNATIONAL APPLICATION NO <b>PCT/EP00/07975</b>	ATTORNEY'S DOCKET NUMBER <b>H 4388 PCT/US</b>			
<p>17. ■ The following fees are submitted.</p> <p><b>Basic National Fee (37 CFR 1.492(a)(1)-(5)):</b> Search Report has been prepared by the EPO or JPO. .... <b>\$890.00</b></p> <p>International preliminary examination fee paid to USPTO (37CFR 1.482) ..... <b>\$710.00</b></p> <p>No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37CFR 1.445(a)(2)) .. <b>\$740.00</b></p> <p>Neither international preliminary examination fee (37CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO. .... <b>\$1,040.00</b></p> <p>International preliminary examination fee paid to USPTO (37CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).... <b>\$100.00</b></p>		CALCULATIONS      PTO USE ONLY			
<b>ENTER APPROPRIATE BASIC FEE AMOUNT</b> =		\$ 890 00			
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date 37 (CFR 1.492(e))		\$			
Claims	Number filed	Number Extra	Rate		
Total Claims	1-20 =1	0	X 18.00	\$	0
Independent Claims	1-3 =1	0	X 84.00	\$	00
Multiple dependent claims (s)(if applicable)		0	+ 280.00	\$	00
<b>TOTAL OF ABOVE CALCULATIONS</b> .....		=	\$ 890 00		
Reduction by ½ for filing by small entity, if applicable Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28).		\$			
<b>SUBTOTAL</b> =		\$ 890 00			
Processing fee of \$130.00 for furnishing the English translation later the <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37CFR 1.492(f)) .....		+ \$			
<b>TOTAL NATIONAL FEE</b> =		\$ 890 00			
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) \$40.00 per property +		\$			
<b>TOTAL FEES ENCLOSED</b> =		\$ 890 00			
		Amount to be refunded	\$-----		
		charged			
a. <input type="checkbox"/> A check in the amount of \$ ..... to cover the above fees is enclosed.					
b. ■ Please charge my Deposit Account No. <u>01-1250</u> in the amount of <u>\$ 890.00</u> to cover the above fees. A triplicate copy of this sheet is enclosed. Order No. <u>02-0107</u> .					
c. ■ The Assistant Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>01-1250</u> . A triplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO	Henkel Corporation, Law Dept. 2500 Renaissance Blvd., Ste. 200 Gulph Mills, PA 19406.....				
 <b>SIGNATURE</b> Kimberly R. Hild NAME ATTORNEY FOR APPLICANT 39,224 REGISTRATION NUMBER					

**JC13 Rec'd PCT/PTO 25 FEB 2002**

PATENT  
Docket No. H 4388 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re Application of:  
Kirsten, et al.**

**International Application No.** PCT/EP00/07975  
**International Filing Date:** August 16, 2000

**Serial No.** To be assigned      **Examiner:** To be assigned  
**Filed:** To be assigned      **Art Unit:** To be assigned

## Title: MICROWAVE BONDING

"Express Mail Post Office to Addressee" service mailing label number EL615775349US

## **PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

**In the Specification (Using the English Translation):**

On page 1 of the English translation, on a separate line between the title and line 1, please insert the following paragraph:

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PCT/EP00/07975**

**-- CROSS REFERENCE TO RELATED APPLICATIONS**

This application is a national stage application under 35 U.S.C. § 371 of international application PCT/EP00/07975 filed on August 16, 2000, the international application not being published in English. This application also claims priority under 35 U.S.C. §119 to DE 199 40 128.4 filed on August 24, 1999.

On page 1, on a separate line after the above inserted paragraph and before line 1, please insert the following header:

**-- BACKGROUND OF THE INVENTION -- .**

On page 2, on a separate line between lines 20 and 21, please insert the following header:  
**--SUMMARY OF THE INVENTION--.**

On page 3, on a separate line between lines 2 and 3, please insert the following header:  
**-- DETAILED DESCRIPTION OF THE INVENTION --.**

On page 9, line 1, please delete the heading “CLAIMS” and insert therefor:  
**-- What is claimed is: --**

On a separate page, after page 10, please insert the enclosed Abstract of the Disclosure.

**In the Claims**

Please cancel Claims 2 to 11, without prejudice.

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PCT/EP00/07975

**REMARKS**

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

**Status of Claims**

Claim 1 will be pending after entry of the present amendment. Claims 2 to 11 are being canceled without prejudice.

**Amendment**

The specification is being amended to insert section headers and an abstract of the disclosure in accordance with 37 CFR §1.77 to better conform with US patent practice. The specification is also being amended to insert a cross-reference to related applications in accordance 37 CFR §1.78 and to claim priority to those applications listed therein.

Attached hereto is a marked up version of the changes made to the specification entitled "Version With Markings To Show Changes Made."

No new matter is added by the amendments to the specification.

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PCT/EP00/07975

**CONCLUSION**

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

*Kimberly R. Hild*  
Kimberly R. Hild  
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Attorney for Applicants  
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*February 25, 2002*  
Henkel Corporation  
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Gulph Mills, PA 19406

**Docket No. H4388 PCT/US  
PCT/EP00/07975**

### **Abstract of the Disclosure**

A process for bonding at least two substrates with a hotmelt adhesive using microwave energy is provided. The process includes applying a microwave-activatable primer to a least one of the substrates and applying a hotmelt adhesive to a least one of the substrates. The method also includes pressing the substrates together so that the microwave-activatable primer and the hot melt adhesive are between the substrates, and exposing at least the microwave-activatable primer to microwaves to heat the hotmelt adhesive. The present invention also provides a process for spraying a hot melt adhesive onto a substrate where the hot melt adhesive includes nanoparticles having ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties.

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**VERSION WITH MARKINGS TO SHOW CHANGES MADE**

**In the Specification:**

On page 9, line 1, the heading "CLAIMS" has been amended as shown below:  
[CLAIMS] What is claimed is:

Rec'd PCT/PTO 31 MAY 2002

PATENT  
Docket No. H 4388 PCT/US

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

**In re Application of:**  
Kirsten, et al.

**International Application No.** PCT/EP00/07975  
**International Filing Date:** August 16, 2000

**Serial No.** 10/069,409  
**Filed:** To be assigned

**Examiner:** To be assigned  
**Art Unit:** To be assigned

**Confirmation No.** 3267

**Title:** MICROWAVE BONDING

"Express Mail Post Office to Addressee" service mailing label number EV 105943565 US

**SUPPLEMENTAL PRELIMINARY AMENDMENT**

Box PCT  
Assistant Commissioner for Patents  
Washington, DC 20231

Attn: DO/EO/US

Sir:

Prior to examining this application, please amend the application as follows:

**In the Claims**

Please cancel Claim 1, without prejudice.

Please add the following new claims:

- 12. (NEW) A process for bonding substrates with hotmelt adhesive comprising:
  - (a) providing at least two substrates for bonding together;
  - (b) applying at least one microwave-activatable primer to at least one of the substrates;
  - (c) applying at least one hotmelt adhesive to at least one of the substrates;
  - (d) pressing the at least two substrates together so that the primer and the hotmelt adhesive are between the substrates and exposing at least the microwave-activatable primer to microwaves to heat the hotmelt adhesive; and
  - (e) cooling the hotmelt adhesive

13. (NEW) The process of claim 12 wherein one of the substrates is porous and the other substrate is porous or nonporous.

14. (NEW) The process of claim 13 wherein at least one of the substrates is a porous woven or nonwoven fibrous substrate selected from leather or a textile.

15. (NEW) The process of claim 12 wherein the microwave-activatable primer comprises a mixture of at least two different microwave-active additives in a quantity sufficient to heat the hotmelt adhesive to where it flows.

16. (NEW) The process of claim 15 wherein the two microwave-active additives differ in at least one property selected from size, shape, electrical conductivity or thermal conductivity, or combinations thereof.

17. (NEW) The process of claim 12, wherein the hotmelt adhesive is thermoplastic or reactive and contains no microwave-activatable additives.

18. (NEW) The process of claim 12, wherein the hotmelt adhesive is applied in a solid or molten state.

19. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied in the form of a film, net or powder.

20. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied as a melt to the substrate.

21. (NEW) The process of claim 18 wherein the hotmelt adhesive is applied by spraying the hotmelt adhesive onto at least one of the substrates.

22. (NEW) The process of claim 12 wherein the applied microwave-activatable primer is exposed to electromagnetic fields of 1 Hz to 100 GHz to improve wetting or penetration or both of the hotmelt adhesive.

23. (NEW) The process of claim 12 wherein the substrates having the liquid hotmelt adhesive and the microwave-activatable primer in between are pressed together under a pressure ranging from 0.5 bar to 6 bar for a time period ranging from 5 seconds to 20 minutes.

24. (NEW) The process of claim 23 wherein the substrates are pressed together under a pressure ranging from 2 bar to 5 bar for a time period ranging from 10 seconds to 30 seconds.

25. (NEW) The process of claim 12, wherein the microwave-activatable primer is exposed to microwaves that heat the primer and not the substrates.

26. (NEW) The process of claim 12 wherein after exposing the microwave -activatable primer to the microwaves, the substrates remain pressed together at least until after the hotmelt adhesive begins to solidify.

27. (NEW) The process of claim 26 wherein the substrates remain pressed together at least until the hotmelt adhesive has cooled to a temperature of about 30°C.

28. (NEW) The process of claim 12 wherein the substrates are components of a shoe and the process is part of an in-line process for making shoes.

29. (NEW) A process for applying hotmelt adhesive comprising spraying hotmelt adhesive to at least one substrate wherein the hotmelt adhesive comprises nanoscale particles having ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties.

30. (NEW) The process of claim 29 wherein the substrate is a component of a shoe. --

**Serial No. 10/069,409  
PCT/EP00/07975**

**Docket No. H4388 PCT/US**

**REMARKS**

Applicants respectfully request the Examiner to enter the above amendments prior to examination of this application.

**Status of Claims**

Claims 12 to 30 will be pending after entry of the present amendment. Claim 1 is being canceled without prejudice.

**Amendment**

New Claims 12 to 30 replace original claims 1 to 11, and are being presented to better conform with US patent practice. These new claims are supported by the specification for example as shown in the Table below (cites to the specification are for the English translation):

<b>Claim</b>	<b>Support in Specification</b>
12	page 2, lines 21 to 30
13	page 1, lines 1 to 3
14	original claim 2
15, 16	original claim 3
17	page 3, lines 15 to 19
18, 19, 20, 21	original claim 5
22	page 5, lines 7 to 9
23, 24	original claim 7
25	original claim 8
26	page 5, lines 23 to 27
27	original claim 9
28	original claim 10
29, 30	page 5, line 27 to page 6, line 9, page 1, lines 1 to 3

No new matter is added by the new claims.

**Serial No. 10/069,409  
PCT/EP00/07975**

**Docket No. H4388 PCT/US**

**CONCLUSION**

Applicants respectfully request early and favorable notification of allowance of all pending claims. The Assistant Commissioner is authorized to charge any deficiency in the required fee or to credit any overpayment to Deposit Account 01-1250 in connection with this amendment.

Respectfully submitted,

*Kimberly R. Hild*

Kimberly R. Hild  
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Attorney for Applicants  
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*May 31, 2002*

Henkel Corporation  
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## Microwave Bonding

This invention relates to a process for bonding porous and/or nonporous substrates with hotmelt adhesives, more particularly in shoe manufacture.

Requirements and specifications for an adhesive in shoe manufacture are described in **EN 522** and **EN 1392**. A particularly important requirement is a high spotting tack which ensures exact positioning, for example of the sole on the shoe base. In addition, the quality/strength of the bond presupposes good penetration/wetting of the substrates to be bonded, particularly where they are porous and above all fibrous. These requirements conflict with one another, particularly where hotmelt adhesives are used. The prior art is based either on amorphous systems or crystalline formulations. Whereas amorphous hotmelt adhesives show adequate spotting tack, their penetration/wetting is unsatisfactory. Where crystalline systems are used, good penetration is generally present whereas their spotting tack for positioning the shoe sole is inadequate. Although amorphous or crystalline hotmelt adhesives can be optimized in regard to the described problems, such improvements are only ever achieved at the expense of the other requirement described above. Optimal spotting tack coupled with optimal penetration/wetting cannot be achieved solely by formulation in accordance with the prior art.

In known processes, the above-mentioned difficulties can only be overcome by additional and expensive process steps. **DE 19504007**, for example, describes the pre-heating or post-heating of substrates to improve the penetration of an amorphous hotmelt adhesive. An alternative way and, in many cases, the only way of obtaining a high-quality bond is the additional application of a primer and/or adhesive layer for carrying out contact bonding (two-way process). In many cases, this means that the

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objective of solventless bonding cannot be achieved.

WO 99/24520 describes a microwave-activatable adhesive which, besides its polymers, additionally contains a mixture of two components which are receptive to microwaves and which - in terms of size, shape and conductivity - are selected to increase the absorption of the microwaves in the polymeric composition. In order to bond wood, plastics and semiconductors to one another, the adhesive is said to be applied to one or both substrates in known manner, for example by spraying, and then exposed to microwave radiation, the adhesive forming a bond. The disadvantage of this adhesive is that it cannot be accurately or constantly applied by spraying and is therefore unsuitable for certain applications, for example in shoemaking for bonding soles.

Against the background of this prior art, the problem addressed by the present invention was to provide a process for bonding porous and nonporous materials where the strength requirements would be safely fulfilled and spray application of the adhesive would be unproblematic.

The solution to this problem is defined in the claims and consists essentially in the fact that the primer and not the adhesive contains additives which are receptive to microwaves and with which the adjacent adhesive layer can be activated.

Accordingly, the present invention relates to a process for bonding porous and/or nonporous substrates with adhesives, more particularly hotmelt adhesives, in which

- a) a microwave-activatable primer is applied to at least one substrate,
- 25 b) an adhesive, more particularly a hotmelt adhesive, is applied to at least one substrate,
- c) both substrates with the primer and the adhesive or the hotmelt adhesive in between are exposed to microwaves and at the same time pressed together and
- 30 d) the microwave-heated adhesive is left to set.

Preferred embodiments of the invention can be found in the dependent claims.

So far as the microwave-active additives are concerned, reference is specifically made to **WO 99/24520** of which the disclosure is hereby included as part of the disclosure of the present invention. In addition, however, it is pointed out that the primer may also contain nanoscale microwave-active additives. In this case, one component is sufficient.

So far as the bonding process is concerned, reference is made to **WO 99/24498** of which the disclosure is also included as part of the subject matter of the present application.

The essential aspects of the present invention are discussed in the following.

The process according to the invention resolves the described limitation in the bonding of shoes.

Accordingly, the process according to the invention is based on the use of thermoplastic and/or reactive adhesive systems which can be selectively activated by electromagnetic radiation through the primary layer. Activation is based on locally defined heating of the primer layer and hence the adjacent adhesive layer. The bonded substrates are heated only slightly and ideally not at all, but at all events more slowly than the modified adhesive system with a microwave-active primer layer and hence are subjected to little or no heat stress. The activation of the adhesive layer through the primer layer in accordance with the invention differs significantly from the conventional activation processes presently used in the shoe industry (for example IR radiation, circulated hot air).

The locally defined heating of the adhesive layer through the primer layer in accordance with the invention is made possible by the modification of standard primers with suitable "signal receivers" which absorb electromagnetic energy, as described in **WO 93/02867**. For shoe adhesives, such signal receivers are, for example, quartz, tourmaline,

barium titanate, lithium sulfate, potassium (sodium) tartrate, ethylenediamine tartrate, ferroelectric materials of perovskite structure and, above all, lead zirconium titanate. Where magnetic alternating fields are used, any ferrimagnetic, ferromagnetic or superparamagnetic materials are basically suitable, more particularly the metals aluminium, cobalt, iron, nickel or alloys thereof and metal oxides of the n-maghemit type ( $\gamma\text{-Fe}_2\text{O}_3$ ) and the n-magnetite type ( $\text{Fe}_3\text{O}_4$ ), ferrites with the general formula  $\text{MeFe}_2\text{O}_4$ , where Me stands for divalent metals from the group consisting of copper, zinc, cobalt, nickel, magnesium, calcium or cadmium. Carbon blacks and carbon fibers are also suitable. In addition, it essentially contains the known components for primers, for example chloramine, chlorinated polyolefins, polychloroprene or polyurethane. These components are preferably selected according to the hotmelt adhesive components and the substrates.

The primer is preferably applied to at least one substrate in the form of a solution or dispersion.

Suitable adhesives are, in principle, any known adhesives providing they are sprayable, more particularly sprayable hotmelt adhesives. In principle, they may contain all the usual polymers. Examples of thermoplastically softenable adhesives are hotmelt adhesives based on ethylene/vinyl acetate copolymers, polybutenes, styrene/isoprene/styrene and styrene/butadiene/styrene copolymers, thermoplastic elastomers, amorphous polyolefins, linear thermoplastic polyurethanes, copolyesters, polyamide resins, polyamide/EVA copolymers, polyaminoamides based on dimer fatty acids, polyester amides or polyether amides. Other suitable adhesives are, in principle, the known two-pack adhesives based on one- or two-component polyurethanes, one- or two-component polyepoxides, silicone polymers (one or two components), the silane-modified polymers described, for example, in **G. Habenicht, "Kleben: Grundlagen, Technologie, Anwendungen"**, 3rd Edition, 1997, Chapter 2.3.4.4. The

(meth)acrylate-functional two-pack adhesives based on peroxidic hardeners, anaerobic curing mechanisms, aerobic curing mechanisms or UV curing mechanisms are also suitable as the adhesive matrix.

The adhesives are preferably low-solvent types, i.e. they contain  
5 less than 1% by weight of organic materials boiling at temperatures below 200°C.

Suitable frequencies for the selective heating of the primer layer are any electromagnetic fields from 1 Hz to 100 GHz. Magnetic alternating fields with frequencies from 10 KHz to 10 GHz are particularly suitable.

10 The process according to the invention counters the known difficulties involved in the use of thermoplastic and/or reactive hotmelt adhesives by the use of a modified adhesive system - applied to one side - of a primer and a hotmelt adhesive with optimized spotting tack, optionally with the additional aid of conventional activation processes, to facilitate  
15 exact positioning, for example of the sole on the shoe base or an inner sole. The composite structure thus produced is then pressed in a device suitable for the process according to the invention and is activated by electromagnetic energy in that state, as described above. In this way, the adhesive layer adjacent the primer layer is crosslinked in a state for optimal  
20 penetration/wetting through the selective heating of the primer layer and hence the adjacent adhesive layer. In this way, the standards laid down in EN 522 and EN 1392 are achieved or surpassed.

In another embodiment of the process according to the invention, the bonded structure is cooled in the pressed state after activation. The  
25 advantage of this is that it eliminates the risk of unwanted opening of the bonded structure - still warm after activation - through recovery forces at work in the shoe material.

The present invention also relates to a process for establishing adhesive bonds by means of electrical, magnetic or electromagnetic  
30 alternating fields, the adhesive layer containing nanoscale particles which

directly heat the adhesive layer under the influence of these alternating fields. The object of heating the adhesive layer in this way is to increase the strength of the bonds through better wetting or penetration by the heated adhesive, more particularly the hotmelt adhesive. The nanoscale 5 particles act as fillers with "signal receiver" properties so that energy in the form of electromagnetic alternating fields is purposefully introduced into the adhesive bond. The introduction of energy into the adhesive results in a considerable local increase in temperature so that the viscosity is reduced.

The process according to the invention is distinguished from the 10 conventional methods of heating by the fact that the heat is generated in the adhesive joint itself and is locally confined thereto and by the fact that the substrate materials to be bonded are subjected to little or no heat stress. The process is very quick and effective because the heat does not have to be introduced into the adhesive joint by diffusion through the 15 substrates. The process according to the invention also considerably reduces heat losses through dissipation or radiation through the substrate so that it is particularly economical. Above all, however, the nanoscale particles at best merely impede but do not prevent spraying of the adhesive melt.

20 Electrical alternating fields or magnetic alternating fields are suitable for the introduction of energy. Where electrical alternating fields are applied, suitable filler materials are any piezoelectric compounds, for example quartz, tourmaline, barium titanate, lithium sulfate, potassium (sodium) tartrate, ethylenediamine tartrate, ferroelectric materials of 25 perovskite structure and, above all, lead zirconium titanate. Where magnetic alternating fields are used, any ferrimagnetic, ferromagnetic or superparamagnetic materials are basically suitable, more particularly the metals aluminium, cobalt, iron, nickel or alloys thereof and metal oxides of the n-maghemite type ( $\gamma\text{-Fe}_2\text{O}_3$ ) and the n-magnetite type ( $\text{Fe}_3\text{O}_4$ ), ferrites 30 with the general formula  $\text{MeFe}_2\text{O}_4$ , where Me stands for divalent metals

from the group consisting of copper, zinc, cobalt, nickel, magnesium, calcium or cadmium.

Where magnetic alternating fields are used, nanoscale superparamagnetic particles, so-called single domain particles, are particularly suitable. Compared with the paramagnetic particles known from the prior art, the nanoscale fillers are distinguished by the fact that they have no hysteresis. The result of this is that the dissipation of energy is not produced by magnetic hysteresis losses, instead the generation of heat is attributable to an oscillation or rotation of the particles in the surrounding matrix induced during the action of an electromagnetic alternating field and, hence, ultimately to mechanical friction losses. This leads to a particularly effective heating rate of the particles and the matrix surrounding them.

Nanoscale particles in the context of the present invention are particles with a mean particle size (or a mean particle diameter) of no more than 500 nm and preferably no more than 300 nm. The nanoscale particles to be used in accordance with the invention preferably have a mean particle size of 1 to 40 nm and more preferably 3 to 30 nm. In order to utilize the effects through superparamagnetism, the particle sizes should be no more than 30 nm. The particle size is preferably determined by the UPA (ultrafine particle analyzer) method, for example by laser light back scattering. In order to prevent or avoid agglomeration or coalescence of the nanoscale particles, the particles are normally surface-modified or surface-coated. A corresponding process for the production of agglomerate-free nanoscale particles, for example iron oxide particles, is described in columns 8 to 10 of **DE-A-196 14 136**. Methods for the surface coating of such nanoscale particles for avoiding agglomeration thereof are disclosed in **DE-A-197 26 282**.

The nanoscale materials are added to the adhesive in a quantity of 1 to 30% by weight and preferably 3 to 10% by weight, based on the

composition as a whole.

In principle, any relatively high-frequency electromagnetic alternating field may be used as the energy source for heating the nanoscale particles. For example, electromagnetic radiation of the so-called ISM (industrial, scientific and medical applications) ranges, i.e. frequencies between 100 MHz and about 200 GHz, may be used, cf. inter alia **Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd Edition, Vol. 15, chapter entitled "Microwave technology"**, for further particulars.

It was pointed out in the foregoing that, where nanoscale particles according to the invention are used, electromagnetic radiation may be used to particular effect. This is clearly reflected in the fact that, even in the low-frequency range of about 50 kHz or 100 kHz up to 100 MHz, virtually any frequency can be used to produce the amount of heat needed to split the adhesive bond matrix in the adhesive matrix. A frequency range of 500 kHz to 50 MHz may advantageously be used. The choice of the frequency may be determined by the equipment available, care naturally having to be taken to ensure that interference fields are not radiated.

The adhesives containing the nanoscale particles may be used with or without primers for bonding porous and/or nonporous substrates because they may readily be applied by spraying.

**CLAIMS**

1. A process for bonding porous and/or nonporous substrates with hotmelt adhesives, in which
  - a) a microwave-activatable primer is applied to at least one substrate,
  - b) a hotmelt adhesive is applied to at least one substrate,
  - c) both substrates with the primer and the hotmelt adhesive in between are exposed to microwaves and at the same time pressed together and
  - d) the microwave-heated adhesive is left to cool.
- 10 2. A process as claimed in claim 1, characterized in that porous substrates, more particularly fibrous substrates, such as leather or textiles in the form of woven or nonwoven materials, are bonded to other porous substrates or to nonporous substrates.
- 15 3. A process as claimed in claim 1, characterized in that the microwave-activatable primer contains a mixture of at least two microwave-active additives differing in size, shape and/or electrical or thermal conductivity in a quantity sufficient to heat the hotmelt adhesive layer to the point where it flows.
- 20 4. A process as claimed in claim 1, characterized in that the hotmelt adhesive is thermoplastic or reactive and preferably contains no microwave-activatable additives.
- 25 5. A process as claimed in claim 1, characterized in that the hotmelt adhesive is applied in the solid state, for example in the form of a film, a net or in the form of a powder, preferably as a melt, above all by spraying.
6. A process as claimed in claim 1, characterized in that the hotmelt adhesive applied is exposed together with the primer and the substrates to electromagnetic fields of 1 Hz to 100 GHz to improve wetting/penetration.
7. A process as claimed in claim 1, characterized in that the substrates with the liquid hotmelt adhesive and primer in between are pressed together under a pressure of 0.5 to 6 bar and preferably 2 to 5 bar for 5

seconds to 20 minutes and preferably for 10 to 30 seconds.

8. A process as claimed in claim 1, characterized in that, through the choice of suitable microwaves, only the primer is heated and not the substrates.

5 9. A process as claimed in claim 1, characterized in that, after their microwave treatment, the substrates are pressed together at least until the hotmelt adhesive begins to solidify, more particularly until the hotmelt adhesive has reached a temperature of ca. 30°C.

10. A process as claimed in at least one of claims 1 to 9 for the manufacture of shoes by the in-line method.

11. The use of an adhesive composition, more particularly a hotmelt adhesive, containing nanoscale particles with ferromagnetic, ferrimagnetic, superparamagnetic or piezoelectric properties for spray application.

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES  
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges Eigentum  
Internationales Büro



(43) Internationales Veröffentlichungsdatum  
1. März 2001 (01.03.2001)

PCT

(10) Internationale Veröffentlichungsnummer  
**WO 01/14490 A1**

(51) Internationale Patentklassifikation<sup>7</sup>: **C09J 9/00**

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(21) Internationales Aktenzeichen: **PCT/EP00/07975**

(22) Internationales Anmeldedatum:  
16. August 2000 (16.08.2000)

(25) Einreichungssprache: **Deutsch**

(81) Bestimmungsstaaten (national): BR, CA, JP, MX, TR,  
US.

(26) Veröffentlichungssprache: **Deutsch**

(84) Bestimmungsstaaten (regional): europäisches Patent (AT,  
BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

(30) Angaben zur Priorität:  
199 40 128.4 24. August 1999 (24.08.1999) DE

**Veröffentlicht:**

— Mit internationalem Recherchenbericht.

Zur Erklärung der Zweibuchstaben-Codes, und der anderen  
Abkürzungen wird auf die Erklärungen ("Guidance Notes on  
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(54) Title: MICROWAVE BONDING

(54) Bezeichnung: MIKROWELLEN-VERKLEBUNG

**WO 01/14490 A1**

(57) Abstract: The invention relates to an adhesive system for bonding open-pored and/or non-porous substrates. Said adhesive system consists of a primer that can be activated by microwaves and of an adhesive, in particular, of a hot-melt-type adhesive. The primer contains two additives which differ in size, shape and/or flowability or thermal conductivity, and which are provided in a quantity that is sufficient for heating the hot-melt-type adhesive to a temperature at which it flows. The adhesive can be applied as usual, especially by spraying, by virtue of the fact that the adhesive preferably does not contain any additives that can be activated by microwaves.

(57) Zusammenfassung: Zum Verkleben von offenporigen und/oder nicht porösen Substraten wird ein Klebstoffsystem vorgeschlagen, das aus einem mit Mikrowellen aktivierbaren Primer und einem Klebstoff, insbesondere einem Schmelzklebstoff besteht. Der Primer enthält zwei Zusätze, die sich in Größe, Form und/oder Strom- bzw. Wärmeleitfähigkeit unterscheiden, und zwar in einer Menge die ausreicht, um den Schmelzklebstoff bis zum Fließen zu erwärmen. Da der Klebstoff vorzugsweise keine mit Mikrowellen aktivierbaren Zusätze enthält, kann er wie üblich aufgetragen werden, insbesondere durch Sprühen.

"Express Mail" mailing label number EV 105943565 US Date of Deposit \_\_\_\_\_

PTO/SB/01 (6-95)

Approved for use through: 10/31/98 OMB 0651-0032

Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE

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0010/PTO Rev. 6/95	U S Department of Commerce Patent and Trademark Office	Attorney Docket Number	H 4388 PCT/US
<b>DECLARATION FOR UTILITY OR DESIGN PATENT APPLICATION</b>		First Named Inventor	Kirsten, Christian
<i>COMPLETE IF KNOWN</i>			
<input type="checkbox"/> Declaration Submitted with Initial Filing	OR	<input checked="" type="checkbox"/> Declaration Submitted after Initial Filing	Application Number
			10/069,409
		Filing Date	
		Group Art Unit	
		Examiner Name	

**As a below named inventor, I hereby declare that**

**My residence, post office address, and citizenship are as stated below next to my name.**

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

## MICROWAVE BONDING

*(Title of the Invention)*

the specification of which

is attached hereto

QB

was filed on (MM/DD/YYYY) **08/16/2000** as United States Application Number or PCT International

Application Number PCT/EP00/07975 and was amended on (MM/DD/YYYY) [redacted] (if applicable)

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment or addendum specifically referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37 Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code §119(a)-(d) or §365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States of America, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or of any PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application Number(s)	Country	Foreign Filing Date (MM/DD/YYYY)	Priority Not Claimed	Certified Copy Attached?
				YES NO
199 40 128.4	Germany	08/24/1999		X

Additional foreign application numbers are listed on a supplemental priority sheet attached hereto

I hereby claim the benefit under Title 35, United States Code §119(e) of any United States provisional application(s) listed below.

Application Number(s)	Filing Date (MM/DD/YYYY)	<input type="checkbox"/> Additional provisional application numbers are listed on a supplemental priority sheet attached hereto

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## DECLARATION

Page 2

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U.S. Parent Application Number	PCT Parent Number	Parent Filing Date (MM/DD/YYYY)	Parent Patent Number (if applicable)
	PCT/EP00/07975	08/16/2000	

Additional U S or PCT international application numbers are listed on a supplemental priority sheet attached hereto.

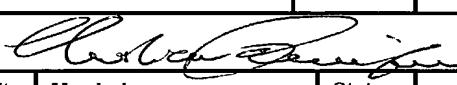
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<input checked="" type="checkbox"/> List Attorney(s) and/or agent(s) name and registration number below			
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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## DECLARATION

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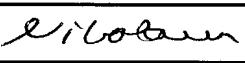
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